AIP Applied Physics Letters

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Citation: Applied Physics Letters **103**, 142404 (2013); doi: 10.1063/1.4823820
View online: http://dx.doi.org/10.1063/1.4823820
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/103/14?ver=pdfcov
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A proposal for an alternative class of spin filter materials: Hybridization-induced high-T_C ferromagnetic semiconductors CoVXAl (X = Ti, Zr, Hf)

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(Received 29 August 2013; accepted 14 September 2013; published online 1 October 2013)

Using *ab-initio* electronic structure calculations, we propose an alternative class of spin filter materials (SFMs) based on the quaternary Heusler compounds CoVXAl (X = Ti, Zr, Hf). We show that the *p-d* hybridization leads to the formation of the ferromagnetic band gap with a moderate exchange splitting ΔE_{ex} and a Curie temperature T_C well above the room temperature. We find that all three compounds are thermodynamically and magnetically stable. Combination of high T_C value together with moderate exchange splitting, as well as crystal structures compatible to the existing semiconductors and metals, makes these compounds promising candidates to find applications as SFMs in spintronics devices. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4823820]

One of the most central challenges in spintronics is the successful injection of spin-polarized current into a semiconductor.[1,2] Several approaches have been applied to achieve it and one of the most promising routes is the use of the so-called spin filter materials (SFMs).[3,4] SFMs are magnetic semiconductors; compounds where there is an energy gap in both spin directions but the band structure is different for the two spin directions leading to magnetic properties. Such materials can be used in magnetic tunnel junctions (MTJs). In usual MTJs, the magnetic electrodes are separated by an insulating barrier and ballistic transport is achieved through the tunnelling of the electrons via the barrier. The alternative is to use a SFM as the barrier and have metallic electrodes. Then the probability for electrons tunnelling through the SFM barrier is different for the two spin-directions and the flow of a spin-polarized current is present.[3,4] Several spin-valve structures based on MTJs incorporating SFMs have been suggested in literature revealing the potential of these compounds[5,6] including also the case of a mixed ferromagnetic (EuO) and usual insulating (MgO) barrier,[7] and of a SFM/silicon contact.[8] Moreover, magnetic semiconductors could find application also in the recently discovered "spin Hall magnetoresistive" devices.[9]

Despite their potential applications, the number of magnetic semiconductors is very limited. The most usual representatives are the europium chalcognides.[10] EuO and EuSe are well-known ferromagnetic and antiferromagnetic semiconductors, respectively.[11] But it is EuS, a ferromagnetic semiconductor, which has been most widely studied.[12,13] Eu chalcogenides crystallize in the cubic rocksalt structure but they have very low Curie temperatures T_C (EuO has the highest T_C of 69.9 K) (Ref. 11) which makes them unsuitable for applications. Other SFMs are the ferrimagnetic $NiFe_2O_4$,[14] $CoFe_2O_4$,[15] and $CoCrO_4$ (Ref. 16) as well as the ferromagnetic $BiMnO_3$ compounds.[17] Among these four compounds, the latter two have very low Curie temperatures. $NiFe_2O_4$ and $CoFe_2O_4$ have very high T_C values of about 800 K but they crystallize in a spinel structure and thus are not easily grown in the form of thin films and this leads to relatively small spin polarization values of the injected current in MTJs based on them; for $NiFe_2O_4$ a value of 22% has been achieved.[14,15] Thus the finding of SFMs suitable for applications is still an open issue.

The aim of the present letter is to search for an alternative class of ferromagnetic semiconductors for spin filter applications in spintronics. Employing *ab-initio* electronic structure calculations within density functional theory, we show that the quaternary Heusler compounds CoVXAl (X = Ti, Zr, Hf) are ferromagnetic semiconductors with a Curie temperature considerably exceeding the room temperature. We reveal that the *p-d* hybridization leads to the formation of the ferromagnetic band gap with a moderate exchange splitting ΔE_{ex}. It is shown that all three compounds are thermodynamically and magnetically stable. Proposed compounds crystallize in LiMgPdSb-type structure, which is similar to the zincblende structure adopted by technologically important semiconductors and which is coherent also to the cubic lattice of most metals. Furthermore, calculated lattice parameters (see Table I) are very close to the ones for well known semiconductors such as InAs (a = 6.06 Å) and AlSb (a = 6.14 Å), which suggests that these ferromagnetic semiconductors could be potential candidates for spin injection into those semiconductors. Note that preliminary results for CoVTiAl have been already published in Ref. 18 and similar compounds have been both theoretically studied[19] and experimentally grown.[20,21]

We employ the full-potential nonorthogonal local-orbital minimum-basis band structure scheme (FPLO)[22] within the generalized gradient approximation (GGA)[23] to calculate the ground state properties. The effective Heisenberg exchange parameters and the Curie temperature T_C are calculated using the formalism already employed in

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TABLE I. Calculated equilibrium lattice constants, formation energy [ΔE_0 (in eV)], magnetic energy [ΔE_m (in eV)], atomic and total spin magnetic moments (in μ_B) for the CoVXAl (X = Ti, Zr, Hf) compounds. Notice that the sequence of the atoms along the diagonal in the cubic fcc unit cell is Co-X-V-Al.

Compound	a(Å)	ΔE_0	ΔE_m	m^{Co}	m^{Y}	m^{V}	m^{Tot}
CoVTiAl	6.04	−1.30	−0.62	0.23	0.32	2.55	3.00
CoVZrAl	6.26	−0.95	−0.73	0.14	0.16	2.78	3.00
CoVHfAl	6.23	−0.98	−0.73	0.16	0.17	2.76	3.00

the case of the usual full-Heusler compounds in Ref. 24. Prior to discussing the origin of the gap we will dwell on the thermodynamic and magnetic stability of the considered compounds. First, since these compounds do not exist experimentally, we have performed total energy calculations to determine their equilibrium lattice constants, which are presented in Table I. All three compounds possess parabolic dependence of their total energy with respect to the lattice constant. Ti, Zr, and Hf have very close atomic radius and the resulting CoVTi(Zr,Hf)Al compounds have lattice constants ranging from 6.04 to 6.26 Å. All three compounds are stable as can be deduced by the formation energies ΔE_0 presented in Table I, which are defined as the difference between the total energy of the compound and the sum of the total energies of the constituents (see Ref. 25 for the exact definition). ΔE_0 is negative meaning that the creation of the compound is favored and the values are about 1 eV. The appearance of a magnetic ground state can be explained in terms of the Stoner criterion. In Figs. 1(a) and 1(b), we present the total density of states (DOS) per formula unit (f.u.) for both a non-magnetic and a magnetic calculation for CoVZrAl, respectively. In the non-magnetic case the Fermi level crosses a pick of the DOS being unstable. The system prefers the magnetic state lowering the number of occupied states around the Fermi level and thus its total energy. In the third column in Table I we present the magnetic energy ΔE_m (in eV) defined as the difference between the magnetic and the non-magnetic state. For all three compounds, we get negative values meaning that the magnetic state is more stable by 0.6–0.7 eV which is a sizeable energy difference.

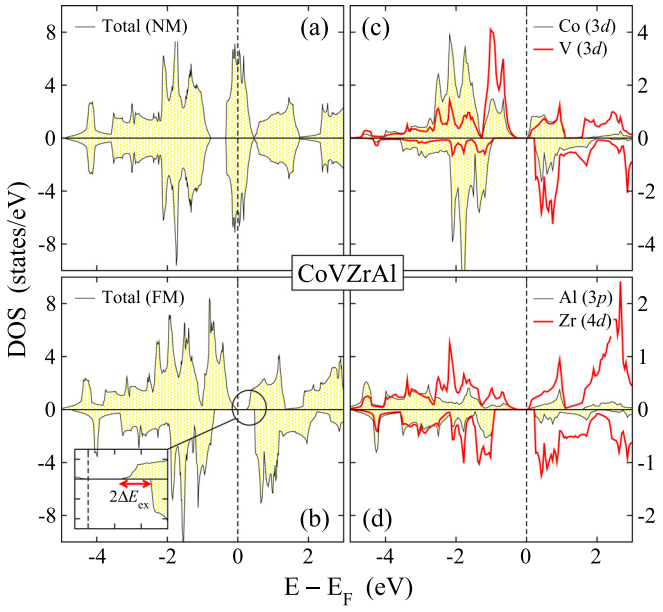

FIG. 1. (a) Total DOS per formula unit for CoVZrAl for the non-magnetic state. (b) The same as (a) for the ferromagnetic ground state. In inset we have enlarged the region around the bottom of the conduction bands and show schematically the exchange splitting $2\Delta E_{ex}$. (c) DOS projected on the valence *d* states of the transition metal atoms V and Co. (d) The same as (c) for the valence *p* and *d* states of Al and Zr, respectively. Note that Fermi energy is set to zero. Positive (negative) DOS values correspond to the majority-spin (minority-spin) states.

All three compounds posses ferromagnetic ground state with a total spin magnetic moment per f.u. of 3.0 μ_B as anticipated by the variant of the Slater-Pauling rule[26,27] discussed in detail in Ref. 18. Each Co (V) atom has four Ti (Zr, Hf) and four Al atoms as nearest neighbors and each Ti (Zr, Hf) atom has four Co and four V atoms as nearest neighbors, and thus the ferromagnetic coupling of the spin moments is expected from the Bethe-Slater curve.[28] Co and Ti (Zr, Hf) atoms carry a relatively small spin magnetic moment since most of the Co 3*d* states are occupied while for Ti (Zr, Hf) most of the valence *d* states are unoccupied. Vanadium atoms, on the other hand, carry almost all the spin magnetic moment which ranges from 2.55 μ_B in CoVTiAl up to 2.78 μ_B in CoVZrAl, and thus the V-V exchange interactions are mainly at the origin of the high Curie temperatures of these compounds as will be discussed later in the letter. We should finally note that the Al atoms carry a vanishing spin magnetic moment and thus we do not include them in Table I.

An important quantity characterizing the SFM is the so-called exchange-splitting ΔE_{ex}. ΔE_{ex} is half the distance between the energy positions of the minimum of the conduction bands of the two spin-directions [see Fig. 1(b)].[29] Two times the ΔE_{ex} is the difference in the barrier which the electrons of different spin character confront when they tunnel from one electrode to the other through the ferromagnetic semiconductor. The largest value and thus the strongest spin filtering effect are expected for CoVZrAl followed by CoVHfAl, as shown in Table II. CoVTiAl has a value of 0.10 eV, less than half the value for the other two compounds. Thus we will use CoVZrAl as the prototype to discuss the origin of the energy gaps in both spin-directions. In Figs. 1(c) and 1(d), we present the DOS projected on the valence states of the four atoms of CoVZrAl and in Fig. 2 we present the band structure along two high symmetry lines in the reciprocal space. Note that the character of a band at the Γ point determines the character of the orbital at the origin of the band in real space. Below the energy window shown in both figures is located a single (per spin) band originating from the 3*s* states of Al which is not relevant to our discussion on the origin of the magnetic semiconducting behavior.

TABLE II. Exchange splitting $2\Delta E_{ex}$ (in eV), first three nearest neighborhood V-V effective Heisenberg exchange parameters (in meV), and mean-field and random-phase approximation estimation of the Curie temperatures (in K) for the compounds under study. Note that number of atoms in each coordination sphere is given in parenthesis.

Compound	$2\Delta E_{ex}$	$J_1(12)$	$J_2(6)$	$J_3(8)$	T_C^{MFA}	T_C^{RPA}
CoVTiAl	0.10	8.95	−3.96	0.21	676	458
CoVZrAl	0.24	10.50	−3.12	0.35	892	652
CoVHfAl	0.20	9.96	−3.09	0.32	834	601

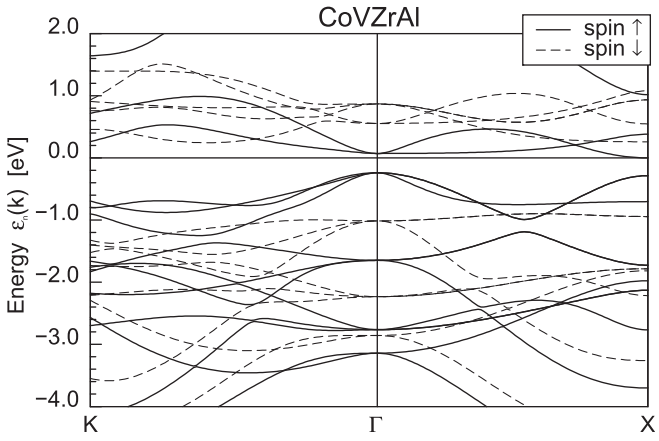

FIG. 2. Spin-resolved band structure of CoVZrAl. The zero energy has been chosen to represent the Fermi level. The solid lines correspond to the spin-up (majority-spin) electrons and the dashed lines to the spin-down (minority-spin) electrons. The deep-lying Al bonding *s* band (originating from the Al 3*s* states in the free atom) is not shown.

We have calculated also the character of all the bands using the so-called fat-band scheme (results are not shown) to reveal their character as in Ref. 30 and in Fig. 3 we present schematically the character of the bands at the Γ point for both spin directions.

In the band structure in Fig. 2 most of the bands are derived from the *d*-orbitals of the transition-metal atoms due to their strong hybridization (see also Fig. 3). The reader is referred to Refs. 18, 26, and 27 for an extended discussion on the hybridization of these orbitals and the origin of the e_g, e_u, t_{2g}, and t_{1u} hybrids since such a discussion is beyond the scope of the present letter. What differs CoVTi(Zr,Hf)Al from other Heusler compounds is the energy position of the Al 3*p*-valence states. In usual Heusler compounds these states are located below the center of the *d*-bands of the transition metal atoms.[18,26,27] This is not the case for the compounds under study. As shown in Fig. 1(d), the Al 3*p* states are located in the same energy window with the *d*-states of the transition metal atoms.

In the majority-spin electronic band structure, the bands due to Al 3*p*-states are located between the double- (e_g) and the triple-degenerate at the Γ point (t_{2g}) bands of the transition metal atoms as shown schematically in Fig. 3 and derived from our fat band type calculations. The t_{2g} and t_{1u}

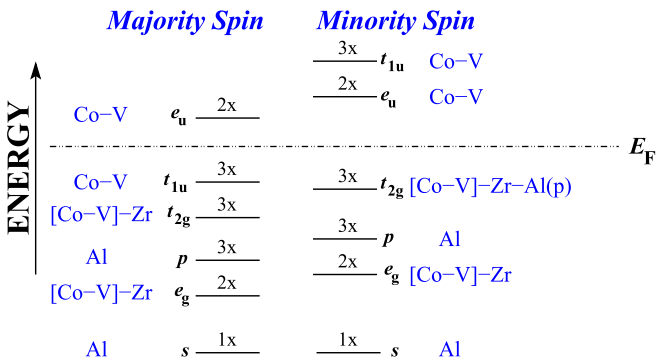

FIG. 3. Schematic representation of the character of the bands at the Γ point. With blue we denote the atoms at the origin of the hybrids creating the band. The factor on top of the lines represents the degree of degeneracy of the band at the Γ point.

bands below the Fermi level have their main weight at the Co and V atoms; away from the Γ point there is also a small Al *p* admixture. The energy gap in the majority-spin band structure is created between the occupied t_{1u} and the unoccupied e_u states.[18] The latter explains why the gap is smaller in the majority spin band structure since the energy splitting between the t_{1u} and e_u states is small.[26]

In the minority spin band structure shown in Fig. 2, the situation is more interesting. The triple degenerate bands just above the e_g states are of Al *p* character followed by the t_{2g} transition metal bands. The latter ones have a very strong admixture of Al *p* states even at the Γ point and thus in the spin down band structure the *p-d* hybridization plays an important role in opening the gap, as in other Al-based transition metal compounds, contributing significantly to the large value of the minority-spin energy gap; it is close to 1 eV.[31] The role of the Al *p* states in opening the gap is confirmed also by calculations where Ga and In substituted for Al. Ga (In) has 4*p* (5*p*) as valence states which are deeper in energy with respect to the valence 3*p* states of Al. This leads to a reduced *p-d* hybridization and thus to smaller energy gaps in both spin directions and our calculations have shown that all CoV(Ti,Zr,Hf)(Ga,In) compounds are spin-gapless-semiconductors; the gap in the majority-spin band structure is of zero width, i.e., the valence and conduction bands almost touch each other.[32]

For realistic applications Curie temperature, T_C, plays a crucial role. Since the V atoms are mainly responsible for the magnetic properties, we take into account only V-V exchange interactions and in Table II we present the first three nearest neighborhood V-V exchange constants. The nearest neighbors V atoms present a strong ferromagnetic coupling with a J_1 value about 10 meV giving a hint that T_C should be also high. Although J_2 is negative these values are smaller than J_1 and ferromagnetism remains robust. Note that the number of atoms within the second coordination shell is also smaller than the corresponding number in first coordination shell (see Table II). Interactions are short ranged, as in usual half-metals,[24,33] and J_3 is almost negligible. Ferromagnetism in the magnetic semiconductors under study could be explained in terms of superexchange interactions similar to the case of (Ga,V)As compounds.[2] Superexchange interactions are short-ranged and favor either ferro- or antiferromagnetism as described by the Kanamori-Goodenough rules.[34,35]

Employing the mean-field approximation (MFA) and random-phase approximation (RPA) methods, we have estimated the Curie temperature T_C. Obtained values are presented in Table II. The RPA method is expected to give T_C values closer to the experimental ones.[24] As seen, the RPA values are about 200 K smaller than the MFA values as for the well-studied usual Heusler compounds in Ref. 24. For CoVTiAl the T_C in RPA is 458 K while when we substitute Zr or Hf for Ti, T_C becomes 652 K and 601 K, respectively. T_C in RPA follows the trends of the vanadium spin magnetic moments shown in Table I. These values are well-above room temperature and thus these compounds should keep a strong ferromagnetic character at the operating temperature of realistic devices. Note that we have also estimated the Curie temperature within MFA taking into account all

possible intra- and inter-sublattice interactions but calculated values are increased by less than 6% with respect to the values in Table II. This behavior is similar to the one observed also in other Heusler compounds like NiMnSb and CoMnSb, in which only one magnetic sublattice is present, i.e., Mn-Mn exchange interactions dominate the magnetic properties. The influence of all other interactions excluding the V-V ones on the calculated values of the T_C is expected to be even smaller within RPA.[24]

In conclusion, using *ab-initio* electronic structure calculations we have proposed an alternative class of spin-filter materials based on the quaternary Heusler compounds CoVXAl (X = Ti, Zr, Hf). We have shown that the *p-d* hybridization leads to the formation of ferromagnetic band gap with moderate exchange splitting. The proposed compounds are found to be thermodynamically stable and show a strong tendency towards ferromagnetism. Furthermore, in terms of crystal structure they are compatible with current semiconductors and metals. The V atoms are mainly responsible for the magnetic properties and the nearest-neighboring V-V interactions stabilize the ferromagnetic order and lead to high values of the Curie temperature. Al atoms play a key role since their valence *p* states are located at the same energy region with the *d* transition metal atoms and in the minority spin band structure they contribute to the large energy gap. Among the three studied compounds, CoVZrAl seems to be the most suitable for applications since it shows the largest T_C combined with the largest value of the exchange splitting. We expect that our results would trigger further interest in incorporating these SFMs as barriers in magnetic tunnel junction based devices.

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